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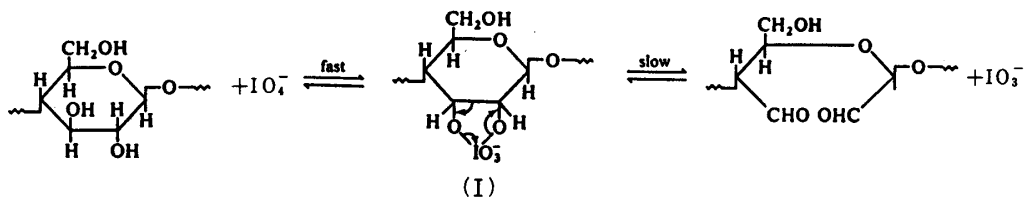
Periodate Oxidation of Mercerized Cellulose and Regenerated Cellulose

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and Tetsuo KOSHIJIMA*

Abstract—Periodate oxidation of commercial cellulose powder, cellulose powder prepared through mercuration with 17.5% aqueous sodium hydroxide, and cellulose powder regenerated as precipitate from the cellulose solution was attempted and compared each other from the point of susceptibility toward oxidation. As a result, chemical evidence was obtained that the different susceptibility to periodate oxidation of various types of celluloses might be ascribable to the variation of non-crystallinity in cellulose.

1. Introduction

The periodate oxidation of cellulose leads to a product called dialdehyde cellulose, which is formed by oxidative cleavage at the C-2 and C-3 of the anhydro D-glucopyranose units in cellulose chains.¹⁾ The oxidation^{1,2)} of 1,2-diol and analogous types occurs through the intermediate ester-ion (I), which decomposes spontaneously by electronic rearrangement to give dialdehyde forms shown as follows.



This reaction proceeds without the simultaneous occurrence of side reaction under the controlled condition of temperature, light, concentration of oxidant, etc. Hydrolysis of the periodate oxidized celluloses gives glyoxal and D-erythrose which was confirmed as D-erythronic acid⁴⁾. This finding proved that periodate oxidation was caused by cleavage of the carbon-carbon linkage containing vicinal hydroxyl groups at the C-2 and C-3 of the anhydro D-glucopyranose units. This evidence also contributed to confirmation of the generally accepted structure of other polysaccharides oxidized with periodate.

In addition to specificity in the oxidative reaction of periodate above mentioned, it is said that the periodate differs from most other oxidizing agents in that

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it has the property to penetrate and react with the crystalline as well as the amorphous portion of cellulose without causing so much degradation under the controlled conditions²⁾. With the common types of oxidizing agents, the reaction is virtually confined to the amorphous regions and the surfaces of the crystallites, and the products suffer unspecific oxidation. Since cellulose is originally not soluble in water, the usual periodate oxidation of cellulose in an aqueous medium is a heterogeneous reaction. However, the reaction proceeds even in an aqueous suspension because of a hydrophilic property of cellulose as its polyhydric alcohols.

Thus, this experiment was attempted to understand the proceeding of periodate oxidation of various types of celluloses. In this report, we have compared the time course of periodate oxidation using commercial cellulose powder with that of cellulose powder worked up chemically.

2. Experimental

2.1 Materials

Whatman cellulose powder CF-1, Merck cellulose powder and Toyo Roshi cellulose powder used in this experiment were purchased from Nakarai Chemicals Ltd., and Schleicher & Schüll cellulose powder from Wako Pure Chemical Industries Ltd. The formers are cellulose powders made from cotton and the latter is that from beech wood pulp. Each cellulose powder was made in the size of 100–200 mesh.

2.2 Preparation of cellulose powder mercerized with aqueous alkali

Cellulose powder (20 g) was added into 17.5% aqueous sodium hydroxide (800 ml) under an atmosphere of nitrogen, and steeped completely in the alkali solution. The content saturated with nitrogen was shielded tightly with a parafilm, and allowed to stand overnight. Cellulose powder swollen in aqueous alkali was collected by suction filtration through a glass filter (G2), and suspended in 10% acetic acid (1 liter). The suspension was stirred slowly for 5 hrs at room temperature. Cellulose powder in aqueous acetic acid was recovered by suction filtration and thoroughly washed with distilled water until the filtrate was no longer acid, and finally with ethanol and acetone, and dried in vacuum. Yield 16.95 g.

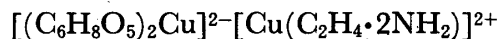
The filtrate and the washings were desalted through dialysis with a cellophane tube toward distilled water, concentrated and freeze-dried to give an amorphous powder of 2.07 g.

2.3 Preparation of regenerated cellulose powders

a) With cupriethylene diamine hydroxide

Cupriethylene diamine solution was prepared by dissolving copper (II) hydrox-

ide in aqueous solution of ethylene diamine according to the preparation method⁴⁾ described by Browing in "Methods of Wood Chemistry". In this case, it is considered that cellulose is dissolved by the formation of the complex as follows:



Commercial cellulose powder (20 g) was added into the newly prepared cupriethylene diamine solution and stirred overnight under an atmosphere of nitrogen. The cellulose-cupriethylene diamine solution was filtered by suction through a glass filter (G2), and cellulose was regenerated as precipitate by pouring the filtrate into 6N hydrochloric acid solution. The precipitate was collected by centrifugation and washed with 2N hydrochloric acid until the supernatant became colorless, then with a mixture of ethanol and water (1 : 1, v/v) until the washings were no longer acid. The aqueous suspension was freeze-dried to give colorless, regenerated cellulose powder of 14.5 g.

b) With 85% phosphoric acid

Commercial cellulose powder (10 g) was mixed in 85% phosphoric acid (500 ml) and dissolved by stirring overnight at room temperature. In this case, cellulose is subjected to swelling and gelatinization in phosphoric acid to give a viscous solution of cellulose. After filtration of the viscous solution through a glass filter (G1) by suction to remove a small amount of insoluble part, regeneration of cellulose was performed by pouring the filtrate into a mixture of methanol and water (1 : 1, v/v). The product was collected by centrifugation, washed with a mixture of methanol and water, repeatedly until the supernatant became neutral, and finally the aqueous suspension was freeze-dried to give colorless, regenerated cellulose powder (8.69 g).

2.4 Periodate oxidation of cellulose powders

Each cellulose powder (2.0 g) suspended in distilled water (100 ml) was oxidized with sodium metaperiodate by shaking at room temperature (15–20°C) in the dark. The amount of periodate used was 1.3 times as much as the theoretical amount (2.64 g) for cellulose powder (2.0 g). The concentration of periodate in a medium was 0.16 mol per liter. The amount of periodate consumed with the course of reaction was determined UV spectrophotometrically by measuring the absorbance at 290 nm of the supernatant liquid of the reaction medium. As reported in a previous paper⁵⁾, the relationship between the values of the absorbance of periodate ion and the amount of periodate indicated a linear reference over a more wide range of the periodate amount, compared with the case of the determination at 223 nm giving absorption maxima of periodate ion. Consequently the use of the absorbance at 290 nm was favorable for the determination of periodate consumed. On periodate oxidation of cellulose, the determination of periodate by UV spec-

trometry is also available as a facile determination method of periodate consumed.

3. Results and Discussion

The time course of periodate consumption on periodate oxidation of commercial cellulose powders from various sources is shown in Fig. 1. The result indicates that the difference on periodate oxidation probably depend on the degree of non-crystallinity of cellulose powder used in this experiment, and therefore, Schleicher & Schüll cellulose powder made from beech wood pulp seems to be more easily subjected to periodate oxidation at the first stage, compared with Whatman cellulose powder and Toyo Roshi cellulose powder which were prepared from cotton cellulose. However, with proceeding of the reaction, Whatman cellulose powder

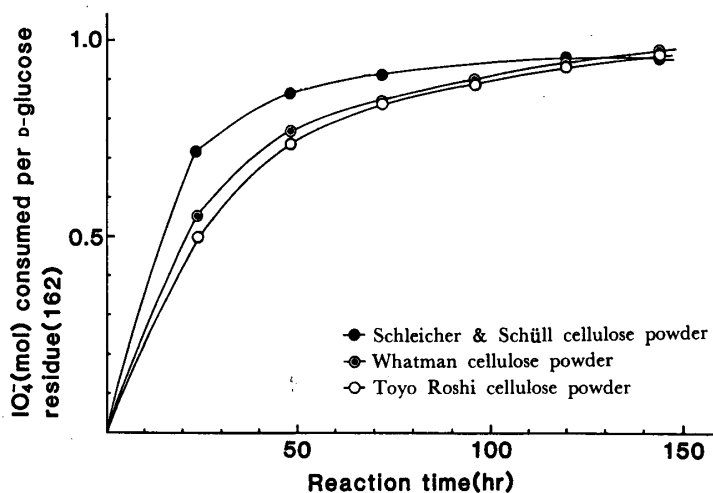


Fig. 1. Periodate oxidation of commercial cellulose powders.

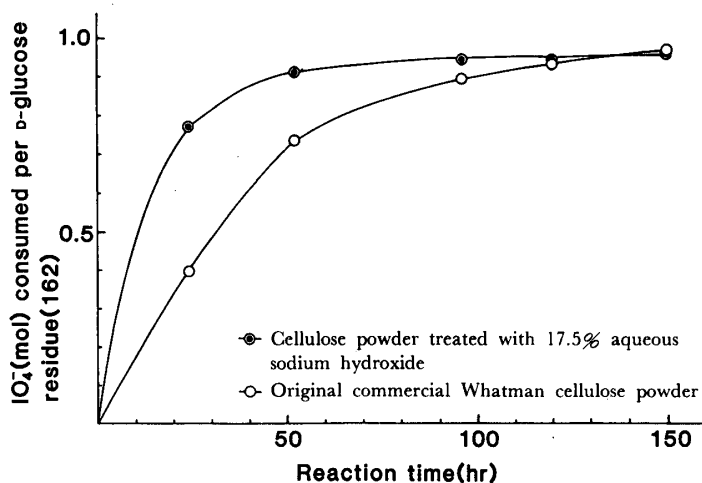


Fig. 2. Periodate oxidation of commercial cellulose powder treated with 17.5% aqueous sodium hydroxide.

has a tendency to be more easily subjected to periodate oxidation than Schleicher & Schüll cellulose powder.

Periodate oxidation of cellulose can be regarded to proceed gradually from the amorphous to the crystalline portion, so that a prolonged reaction time may be necessary to become accessible upto the inner microcrystalline region of cellulose. Actually, in order to reach nearly 100% oxidation level, the reaction mixture of commercial cellulose powders for periodate oxidation required successive shaking during at least more than 150 hrs at room temperature in the dark. However, in the case of cellulose powder mercerized with concentrated alkali or regenerated cel-

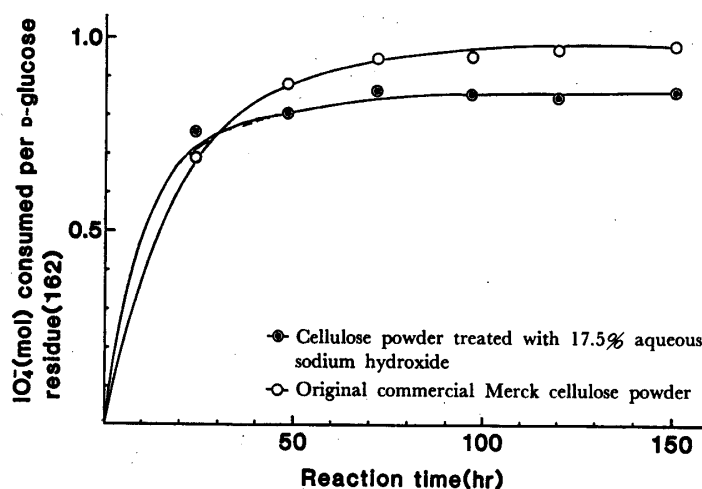


Fig. 3. Periodate oxidation of commercial cellulose powder treated with 17.5% aqueous sodium hydroxide.

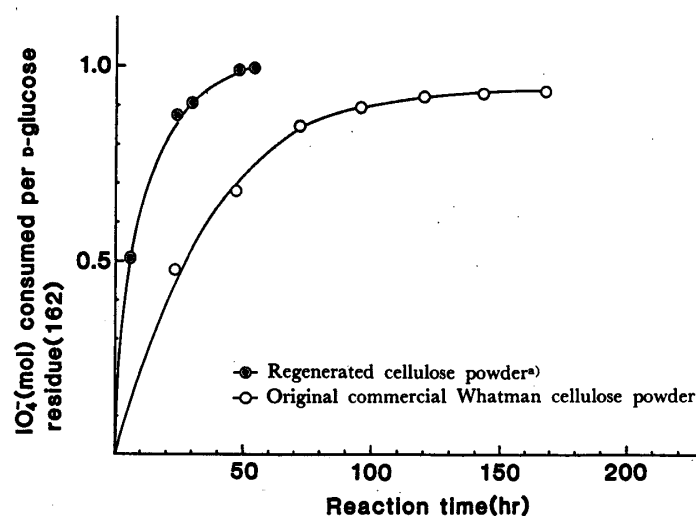


Fig. 4. Periodate oxidation of regenerated cellulose powder prepared from commercial cellulose powder. a) See Experimental 2.3 on the detailed preparation.

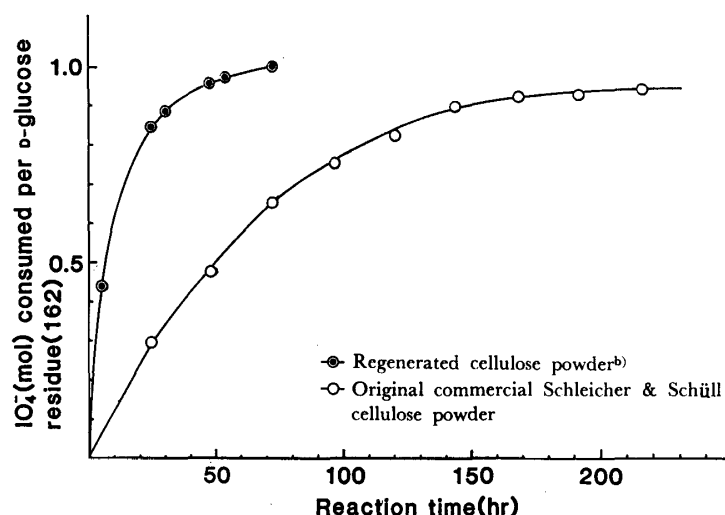


Fig. 5. Periodate oxidation of regenerated cellulose powder prepared from commercial cellulose powder. b) See Experimental 2.3 on the detailed preparation.

lulose powder, enhancement of accessibility of periodate due to the increasing of amorphous portion is expected, and consequently the time to reach the theoretical oxidation level was shortened as shown in Fig. 2, 3, 4 and 5. Especially, periodate oxidation of regenerated cellulose powder shortened the time of one third as observed in Fig. 4 and 5. This means that the time to reach the theoretical oxidation level requires shaking of 150 hrs on periodate oxidation of commercial cellulose powder, but on the case of regenerated cellulose powder it is enough with shaking of 50 hrs. Cellulose powder mercerized with concentrated alkali is more easily subjected to periodate oxidation at the first stage as shown in Fig. 2 and 3, but it is assumed to result in the formation of the resistant portion toward periodate oxidation because 5–10% of non-oxidizable portion is present in mercerized cellulose powder.

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